

Welcome to the world of shock-induced chemistry. Like the wild American West of days long gone, this world is a wide-open frontier—a chemical frontier of unknowns, governed by its own set of rules. Because of the environmental extremes, molecules on the frontier are slammed together with great energy and squeezed atypically close to one another at very high temperatures, allowing them to undergo reactions that would simply never happen under more benign conditions.

Intrigued by these reactions and their molecular offspring, Los Alamos researcher Dana Dattelbaum and her colleagues have staked a claim on the frontier. Their research has several goals, including gaining a comprehensive understanding of how explosives (or other materials) react when shocked and defining the rules so that new molecules can be designed. Another effort explores how extremely high temperatures and pressures, regardless of how they are generated, can be used to create novel new materials.

Synergystic with the experimental work is the development of computer simulations that shed light on how and why the molecules behave as they do under shock conditions. So far, the programs have been remarkably successful at reproduc-

ing the experimental results. Just as important, the simulations are allowing researchers to splice together data taken on vastly different time and distance scales and to construct a consistent picture of how an explosive works. This raises the possibility that someday soon computers will do much of the exploring and will be able to guide the experimentalists down promising research paths.

Getting to know you

Humankind has tinkered with explosive compounds for more than a millennium—references to gunpowder date to 9th century China—yet researchers still don't have a firm understanding of the chemistry that drives the explosion.

What is known is that the explosion is initiated by an impulse, either mechanical or electrical, that sends a shock wave racing through the material at a few thousand meters per second. Ahead of the shock wave lies the undisturbed explosive material at ambient conditions, while behind the shock wave front, or simply the front, is a high pressure, high temperature environment that compresses and instigates the burning of fresh material overrun by the front—the chemical-reaction zone. Through a series of chemical reactions, the high-bond-energy, marginally stable explosive molecules are broken down into stable, lower-bond-energy molecules, such as solid carbon or gaseous carbon monoxide, carbon dioxide, nitrogen, and water vapor. Energy is released in the form of heat and fast-moving reaction products, which increases the pressure and temperature behind the front.

In a non-explosive material, the energy released is either insufficient or released too slowly to sustain the shock, so that the pressure decreases behind the front even as reactions continue. The initial shock wave dies out. But in an explosive material, the

By simply following the atoms as they move about, a quantum molecular dynamics (qMD) simulation can reproduce and predict the properties of a material so well that even Aristotle, who never ascribed to the notion of atoms, would

have been compelled to reconsider his position. Unfortunately, quantummechanics-based qMD simulations, while extremely accurate, have some well-known and serious limitations that, through a series of remarkable and significant developments, Laboratory theorists Anders Niklasson and Marc Cawkwell have largely overcome.

A qMD simulation starts with a physically interesting arrangement of atoms and electrons as an initial condition. One calculates the force on each

atom due to the electrons

and all the other atoms in the arrangement, then uses the force to update the position and velocity of each atom after a tiny increment of time (the time step) has passed. This

procedure is repeated over many thousands of time steps until the desired simulation time is reached. Insomuch as the initial arrangement of atoms reflects their configuration in a real material, the collective response of the atoms reveals the material's behavior.

Typically, the number of calculations needed to determine the atomic forces increases precipitously with the number of atoms and electrons in the simulation, and even on the fastest supercomputers a simulation can very quickly become intractable. Research groups often find themselves running qMD simulations with fewer than 100 atoms, severely limiting the types of behaviors that can be studied.

Now the inter-atomic forces are calculated in qMD from the potential energy of the positively-charged atoms and swarming, negatively-charged electrons, with the energy carried by the electromagnetic field generated by those particles. In turn, the potential energy is calculated in a sort-of numerical yin-yang by first making a good guess of the overall electromagnetic field, then figuring out the quantum state of electrons within that field, and finally by checking

liberated energy exceeds what is needed. The initial disturbance becomes a detonation wave, essentially a shock wave that continues to be driven by the chemical reactions occurring behind the front as the front races through new material. The reaction products cause the material to catastrophically blow apart.

This broad-brush description, while interesting, lacks detail. How exactly does the explosive material burn? By which reactions? At what rates? How much energy is released and how quickly? How are non-energetic molecules affected by the shock wave, and what kind of chemistry do they participate in? If the composition of the explosive is modified, how will that affect the sensitivity and the performance of the explosive? Scientists have few answers to these questions.

"We know the starting molecules and have some idea of the final reaction products based on chemical equilibrium," says Dattelbaum. "Other than that, we know very little about the shock-induced chemical reactions behind the front and almost nothing about the details. We don't even know the general principles that are at work. That makes for challenging, incredibly exciting research."

The research is not just exciting; it's necessary. Consider that with a velocity of a few kilometers per second, a shock wave will propagate on the order of several meters in the few milliseconds it takes for the material to explode. Thus, the shock will interact with and affect material structures on every length scale, from the atomic-scale crystal lattice to the micron-scale crystal grains, up to and including bulk-scale cracks, voids, material interfaces, and domains. In particular, it affects and is affected by structures on the sub-millimeter, or mesoscopic, scale—the same structures that affect and control bulk material properties such as strength, the propagation of cracks, alloy properties, etc. Understanding how an explosive works is tied to the much broader picture of what makes materials "work."

Unfortunately, the physics community doesn't have a firm grasp on the physics of the mesoscale and has had only limited success simulating materials on that scale. That may no longer be the case, however. In a significant breakthrough, Los Alamos theorists Marc Cawkwell and Anders Niklasson have been able to vastly increase the size of molecule-based

to see that the field produced by this electron state is consistent with the assumed initial field. New guesses are refined over and over until an optimum potential is achieved. The process is known as self-consistent-field (SCF) optimization. It needed to be done for every time step, and it was one of the computational bottlenecks of a qMD simulation.

Niklasson and Cawkwell recognized that by introducing an auxiliary electron population to the calculations along with a slightly modified formulation of the inter-atomic forces, the SCF optimization and its gluttonous eating of computer cycles could be eliminated entirely from the computer code. Furthermore, the new formulation was amenable to "fast solver" techniques that slashed the number of numerical operations needed to solve the force equations.

When all the i's were dotted and the t's crossed, the two theorists had demonstrated a turbocharged simulation method that was just as accurate as an "exact" gMD formulism. Most significantly, they proved that it was possible to run a qMD simulation with millions of atoms on large parallel supercomputers with

no loss of accuracy. Their work was selected as an Editor's choice of the prestigious Journal of Chemical Physics for 2012.

Niklasson and Cawkwell have developed a new quantum molecular-dynamics code, LATTE (Los Alamos Transferable Tightbinding for Energetics), which has already been used to predict the chemical reactivity and spectral features of organic materials under shock conditions. They were able to build their material with an unprecedented number of atoms

and so run gMD simulations that revealed large-scale material behaviors. For the first time, reserchers were able to verify and correlate experimental results obtained under vastly different conditions. Not only is this leading to a unified picture of how an explosive works, but in a more general context, to a greater understanding of materials that even Aristotle would have relished.

Snapshot of the chemical frontier, obtained from a LATTE simula-

tion of shock-induced chemical reactions in liquid formic acid.

simulations of materials without breaking the computational bank, setting the stage for a quantum-based molecular dynamics simulation of mesoscale physics. (Read about their work in "Latte" above.)

Explosive program

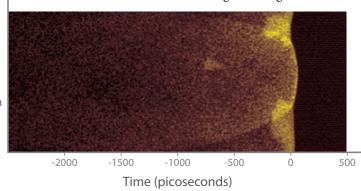
Dattelbaum's team is trying to fill in many of the gaps in our understanding of complex materials by studying simple molecules, both energetic and inert, and removing microstructure from the equation. The team uses two methods to launch well-defined shock waves into the materials—a unique, large-bore, two-stage gas gun and high repetition-rate, pulsed lasers. They then use a variety of diagnostics to quantify the chemistry that occurs following shock compression.

In the first method, a large gas-driven gun fires a projectile into a plate covering the material of interest, which gets shocked by the collision. Something on the order of 100,000-1,000,000 atmospheres of pressure (roughly between 7 and 70 percent of the pressure at the center of the earth) can be achieved, with the pressure remaining at some high level for several millionths of a second.

A density plot of a shock front, similar to what one might see using proton radiography, from a large simulation using several million molecules. Unreacted material is dark brown (positive times). The yellow regions are the high density detonation shock front, followed by regions of darkening brown as the reaction completes and the product gases expand.

In the second experimental method, the team focuses a high-power laser on a metal plate that is bonded to the material. The plate gets very hot very quickly and rapidly expands, sending a shock wave into the material. The maximum pressure achieved is tied to the laser power and overlaps what can be achieved with the gas gun. In contrast to the gas gun experiments, the pressure behind this front reaches its maximum in just a few picoseconds (10⁻¹² seconds), then fades relatively quickly. Using both methods, the group is able to obtain information about both the short- and long-time evolution of the shock-induced chemistry.

By using embedded electromagnetic gauges, the team is able to study reactions occurring behind the front on timescales ranging from tens of nanoseconds to several microseconds. First used by Russian scientists in the 1960s, the tiny, foil-like metal sensors are inserted directly into the explosive. A magnetic field is generated around the sample by an electromagnet, so when the shock wave compresses the material, the metal sensors move through the magnetic field,



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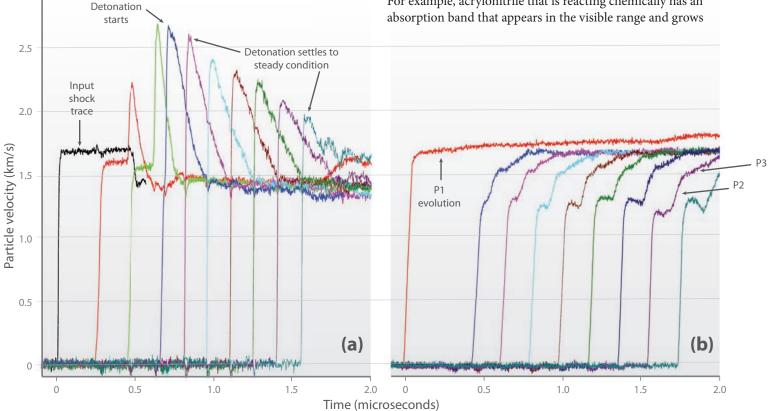


Los Alamos scientist Dana Dattelbaum, seen here at the end of a large gas gun (which extends backwards all the way to the rightmost researcher). The gas gun is one of several pieces of equipment used by Dattelbaum and co-workers Steve Sheffield, Shawn McGrane, Nhan Dang, and Josh Coe in the study of shock phenomena.

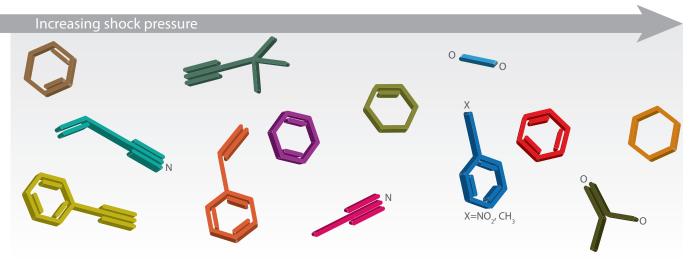
generating a voltage that is proportional to the material's mass or particle velocity. The technology was perfected at Los Alamos, which is currently the only place in the United States where it's used. When combined with other diagnostics, such as optical velocimetry, the team is able to measure the wave dynamics associated with reaction chemistry, including the buildup to detonation, and to probe the reaction zone behind the detonation front during a brief time window.

Of note is that different materials react in different ways under shock loading. In contrast to explosives, many materials, such as the prototypical organic molecule benzene, and many of the polymers used in defense and weapons applications do not release enough energy to drive the shock front when they react. Furthermore, the reactions result in products that are denser than the starting material.

Studying the various reactions often requires a diagnostic that can probe the system on trillionth-of-a-second timescales. Absorption and vibrational spectroscopy fit the bill. For example, acrylonitrile that is reacting chemically has an absorption band that appears in the visible range and grows



(a) The graph shows data from a series of gauges inserted at specific points within nitromethane, a water-like, yet flammable, liquid. As the shock wave moves through the series, each gauge produces a trace of particle velocity, which is proportional to the pressure. The pressure behind the front is seen to build above that of the initial shock (black trace) until, at detonation, the burning of fresh material becomes the driver of shock propagation. (b) Dattelbaum and her team have discovered evidence for intermediate products, such as polymers, forming behind the shock front from simple molecules. Phenylacetelyne, shown here, is seen to produce a pronounced three-wave structure, indicating an intermediate is formed on the way to the final products.



Dattelbaum's group has established an order of shock reactivity for simple chemicals, which they include in what they call their "shock chemistry handbook." As the pressure from a shock wave increases (arrow), the energy available for bond-breaking increases and different kinds of molecules become reactive. The general sequence of bond-breaking begins with carbon-carbon triple bonds (at roughly 5 gigapascals of pressure), and progresses through, for example, carbon-carbon double, carbon-nitrogen triple, oxygen-oxygen single, and carbon-carbon single bonds (at greater than 20 gigapascals).

as a function of time as the chemical conversion proceeds. By combining ultrafast absorption spectroscopy with shock compression techniques, the team has been able to directly measure changes in absorption properties of the chemical intermediates.

Exciting research

Thanks to the healthy experimental program, Dattelbaum and colleagues are slowly writing the book on the chemistry behind the front: what it takes to initiate chemical reactions, how the reactions proceed, the stability of the reaction products, etc. Then in conjunction with state-of-the-art with computer simulations, more complicated reactions can be analyzed in terms of the guiding principles established for the basic reactions.

"If the principles of shock-driven reactivity were better understood, including how they translate to explosive crystals, they may be applied to the design of insensitive explosives," says Dattelbaum, referring to materials that detonate and explode normally, but which are difficult to initiate. At the national laboratories, a goal is to create a new type of insensitive explosive that is nearly impossible to initiate except under very specific and controllable circumstances. "That's the holy grail, because such a material would greatly enhance the safety margin for all applications of chemical explosives, from ammunition to demolition, mining, and even nuclear weapons."

One could envision creating this new insensitive explosive by designing the first bond-breaking step to have a high-activation barrier, or by incorporating functional groups into the explosive molecule that will hold the molecule together,

allowing it to break only under higher pressure and temperature conditions. The molecule overall would still decompose energetically to detonation products once initiated.

At present, there isn't a research group in the world that can accurately predict the sensitivity of an explosive formulation *a priori*. But the team is closer than ever in being able to predict thresholds for shock-driven reactions, including the shock sensitivities of explosive molecules, and is quantifying reaction rates as a function of shock pressure and temperature. Dattelbaum is confident that they will soon be able to recognize promising candidates for an insensitive explosive.

Lastly, Dattelbaum would like to see a robust program of novel-material research and development. Novel polymers are already being considered for body armor, and shockwave dissipating foams have been developed that absorb the shock of a nearby explosion and so protect structures from a terrorist threat. Those novel materials were not created in the throes of an explosion, but extreme conditions can be used to create new states of matter and new molecules that are semi-stable under normal conditions. Could shock-induced chemistry or other extreme techniques become a means to produce the novel materials of the future?

We'll have to wait to see. Still, these explorations of the chemical frontier could not be more timely or appropriate. New techniques that enable pioneering scientists to probe reactions at shorter length and time scales and in harsh conditions are being combined with molecular dynamics simulations that can predict the chemistry and elucidate experimental results. The prospects for interesting science are almost as great as the desires of the scientific frontiersmen to bring the chemistry from behind the front to the fore. LDRD

—Jay Schecker